# Current Sources of Carbon Tetrachloride ($CCl_4$) in our Atmosphere

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## Tweetable Abstract

We update bottom-up sources of the banned ODS and GHG carbon tetrachloride to be 15-25 Gg/year - much closer to observation-based values.

## Abstract

Carbon tetrachloride ($CCl_4$ or CTC) is an ozone-depleting substance whose emissive uses are controlled and practically banned by the Montreal Protocol (MP). Nevertheless, previous work estimated ongoing emissions of 35 Gg/year of $CCl_4$ into the atmosphere from observation-based methods, in stark contrast to emissions estimates of 3 (0-8) Gg/year from reported numbers to UNEP under the MP. Here we combine information on sources from industrial production processes and legacy emissions from contaminated sites to provide an updated bottom-up estimate on current CTC global emissions of 15-25 Gg/year. We now propose 13 Gg/year of global emissions estimate of come from unreported non-feedstock emissions from chloromethane and perchloroethylene plants as the most significant $CCl_4$ source. Additionally, 2 Gg/year are estimated as fugitive emissions from the usage of CTC as feedstock and possibly up to 10 Gg/year from legacy emissions and chlor-alkali plants.

## Introduction:

Carbon tetrachloride ($CCl_4$ or CTC for short and used hereafter) is an ozone-depleting substance (ODS), a greenhouse gas [*WMO*, 2014], a toxic substance at high concentrations, and a carcinogen [*MAK coll.*, 2012]. Being a major contributor to stratospheric ozone depletion, its production and consumption are controlled under the Montreal Protocol's Article 2D, which was agreed to at the June 1990 Meeting of the Parties in London and came into force in 1995. Further adjustments to the Protocol led to a 100% reduction of CTC production and consumption for emissive uses from 2010 onwards. As a consequence of the Montreal Protocol, global atmospheric levels of CTC are steadily decreasing [*Carpenter and Reimann*, 2014].

Although CTC production and consumption for emissive uses is now fully controlled, *Carpenter and Reimann* [2014] reported that CTC emissions to the atmosphere seem to have continued since the full controls were implemented in 2010. This 2014 report, which estimated a 57 Gg/year CTC discrepancy between report based emissions (*i.e.*, bottom-up) and emissions derived from atmospheric observations (*i.e.*, top-down), was the most recent

from a number of reports in the *UNEP/WMO Scientific Assessments of Ozone Depletion* [1999, 2003, 2007, 2011]. These large observation-based emissions contrast to small emissions (3(0-8) Gg/year) inferred from mandated reports to the United Nations Environment Programme (UNEP) under Article 7 of the Montreal Protocol from its signatory parties.

As a consequence of this discrepancy, and the potential omissions to reporting of CTC emissions under the Montreal Protocol, a focused report was instigated to identify the cause of the CTC emissions discrepancy [*SPARC*, 2016]. In this report, new findings led to lower calculated CTC losses in soils and the ocean, reducing the global top-down emissions estimate to about 40 Gg/year. Furthermore, global CTC emissions of about 30 Gg/year were estimated by the difference in CTC levels between the Northern and Southern hemispheres. *SPARC* [2016] merged these results to estimate that current top-down CTC emissions to the atmosphere are 35±16 Gg/year.

Under Article 7, the Montreal Protocol requires each Party to report annually on CTC amounts produced to be used as feedstocks, amounts destroyed, imports and exports. It is important to note that these reported amounts do not represent emissions, but can be used (with reasonable assumptions) to estimate emissions. *Montzka and Reimann* [2011] used the UNEP reports to derive bottom-up CTC emissions by differencing the feedstock sum and amounts destroyed, with estimated emissions as a small proportion of both feedstock usage and reported destruction. In *SPARC* [2016], a re-evaluation of these Article 7 reports yielded CTC emissions of approximately 3 (0-8) Gg/year for the post-2010 period.

The difference between the *SPARC* [2016] top-down 35±16 Gg/year and the Article 7 report-based 3 (0-8) Gg/year emissions estimates suggests that there are on-going unidentified CTC emissions sources. Herein, we seek to identify current CTC sources and evaluate their potential magnitudes. The paper elaborates these sources and potential emissions pathways in the following order: A) production and use of chlorine gas, B) production of CTC, C) usage of CTC, and D) contained stocks or legacy emissions. A summary of the different sources is shown in Figure 1.

## A. Chlorine gas production and usage

The first potential CTC emissions pathway is related to the production of chlorine in chlor-alkali plants (see Figure 1, left side in green). This is due to the relative ease with which hydrocarbons are chlorinated, thus CTC might be formed in many chlorination procedures and released into the environment, to the atmosphere or into surface water.

These chemical production facilities produce chlorine, hydrogen and alkali (sodium or potassium hydroxide) by electrolysis of a salt solution. The main technologies applied to chlor-alkali production are mercury, diaphragm and membrane cell electrolysis, mainly using sodium chloride, or to a lesser extent potassium chloride, as feed. Currently, the chlor-alkali process produces 97% of the world's chlorine [*Brinkmann et al.*, 2014] and the process technologies employed are not specific to geographical regions. In 2012, global chlorine production capacity was estimated to be 76,800 Gg [*Brinkmann et al.*, 2014]. Of the world chlor-alkali capacity, more than 80% is concentrated in three regions; East Asia (48%), North America (19%), and Western Europe (16%) [from *Brinkmann et al.* [2014] Fig. 1].

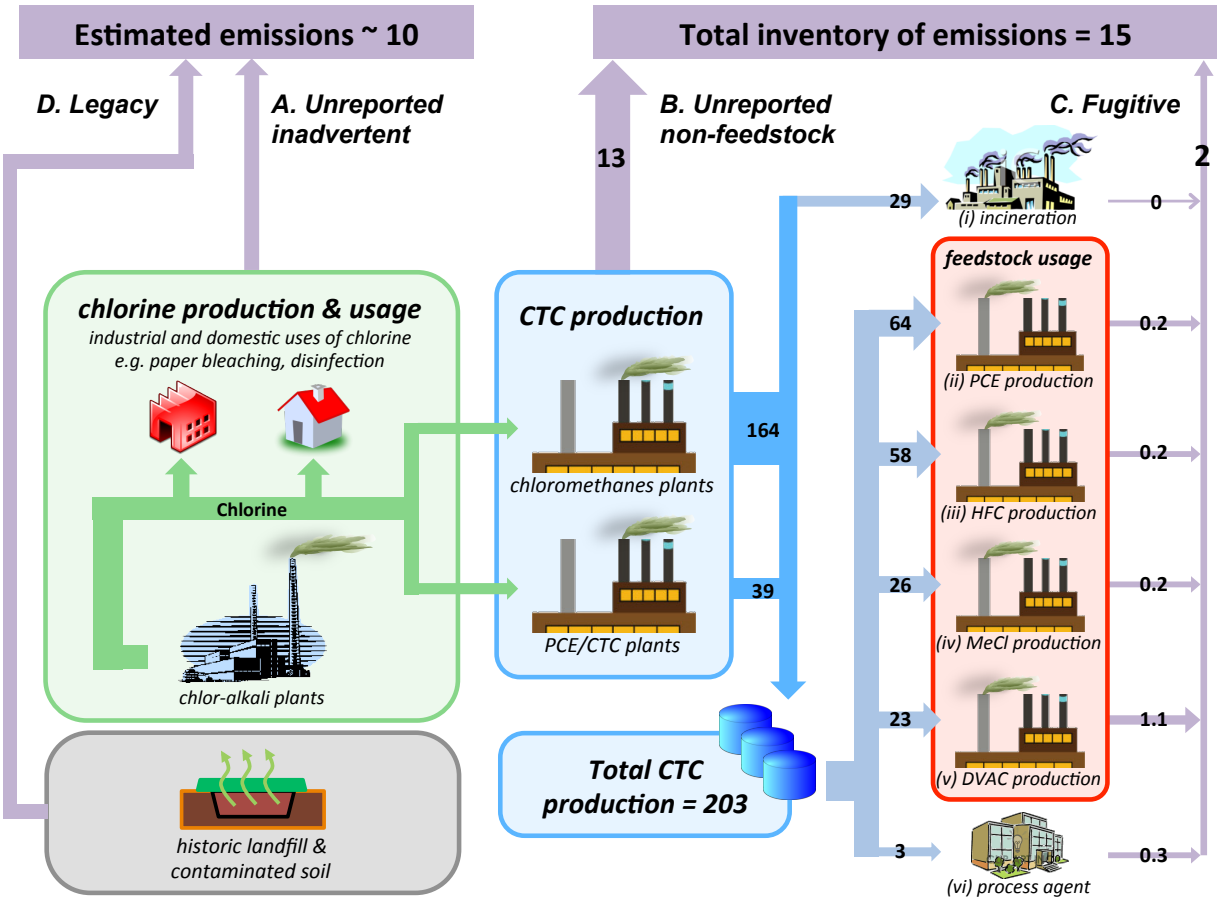


***Figure 1.*** *Schematic of CTC routes from production and use of chlorine ($Cl_2$) gas in chlor-alkali plants (left) to CTC production (middle) to usage (right) and finally, to emissions (top) (in Gg) for 2014. Production and use of chlorine gas ($Cl_2$) are shown in green arrows. The numbers given are 2014 estimates for industry CTC production (blue box and arrows) and use (bluish gray arrows), and emissions amounts of CTC (purple arrows, see Table 1). This 2014 estimate of 203 Gg CTC production is in close agreement with MP Parties' reports to UNEP of 200 Gg in 2013. Feedstock uses of CTC are in red (ii. PCE is perchloroethylene, iii. HFC is hydrofluorocarbon, iv. MeCl is methyl chloride, and v. DVAC is divinyl acid chloride). Emissions are shown as purple lines from: A. unreported inadvertent chlorine gas usages, B. unreported non-feedstock from CM and PCE plants, C. fugitive emissions from contained usages, and D. legacy emissions from landfills and contaminated soils.*

***Unreported inadvertent emissions from chlorine production and usage (Fig. 1, Pathway A):***

Although a potential CTC emissions source from these chlor-alkali plants has not been independently tested nor quantified, unreported inadvertent emissions into the atmosphere could possibly occur during the production of chlorine gas, or from industrial and domestic use of chlorine, *e.g.*, paper bleaching, disinfection (Fig. 1, left side, emissions Pathway A). *Fraser et al.* [2014] used observations in an urban environment to estimate potential global emissions which could include this specific source, in addition to CTC legacy emissions. Although measurements cannot separate this source from legacy emissions, a combined emission estimate of as high as 10 Gg/yr is possible (see section D). *Hu et al.* [2016] also suggested that chlor-alkali plants might be a source of CTC and that the majority of U.S.

emissions appear to be related to industrial sources associated with chlorine production and processing. However, the process of how CTC is formed remains unclear.

Note that CTC is also used as a process agent in the chlor-alkali plants for the elimination of nitrogen trichloride ($NCl_3$) and the recovery of chlorine from tail gases. Worldwide, only a very small fraction of the chlor-alkali plants (nine in 2006) are reported to use CTC as a process agent. The emissions rate from this route is small: 0-30 gram CTC per ton of annual $Cl_2$ capacity. Total fugitive emissions of CTC from the use of CTC as a process agent are included in Table 1 and Fig. 1 (vi, bottom right, Pathway C) and are accounted differently from the unreported inadvertent emissions from chlor-alkali plants (Fig. 1, Pathway A).

## B. CTC production

CTC is produced by two methods (see Fig. 1, middle, Pathway B). First, CTC is a co-product of the industrial production of chloromethanes, including the mono-, di- and tri-chloromethanes ($CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$, hereafter referred to as 'CMs') in CM plants. Second, CTC is also co-produced with perchloroethylene (PCE) in PCE/CTC plants.

***CM plants:*** CMs are produced by hydrochlorinating methanol ($CH_3OH$) with HCl ($CH_3OH + HCl \rightarrow CH_3Cl + H_2O$) to form methyl chloride ($CH_3Cl$), and with subsequent chlorination (*e.g.*, $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$) to produce a series of other important chloromethanes ($CH_2Cl_2$ and $CHCl_3$) as well as CTC. Global chloromethanes (CMs) production in 2014 was 2785 Gg. Older technology tended to produce ~6-8% CTC of the total CMs, together with some heavier chlorocarbons, specifically hexachlorobenzene ($C_6Cl_6$) and hexachlorobutadiene ($C_4Cl_6$). These heavy products, together with some CTC, accumulated as tars, can be refined to produce CTC for chemical intermediate use. Newer technology (*e.g.*, as used in China) generally yields about 4% CTC. An average 4% on the CTC/CM production number is the absolute minimum for CTC generation and is used as the default. In some plants/regions, the CTC/CM production percentage is greater than the default 4%, either because of older equipment or because CTC product is actually required from the process.

***PCE/CTC plants:*** The PCE/CTC process made both products until the mid-1990s, when low CTC demand and strict regulations resulted in the complete closing of plants in developed countries, or investments in plants to run to 100% PCE and zero CTC. The reaction to generate PCE and CTC, by chlorinating a hydrocarbon such as propene, is a chemical equilibrium, and any CTC produced can be separated and either recycled into the reactor to be converted to PCE or can be sent directly to on-line thermal oxidizers or kilns for destruction (Source: multiple discussions over years with producers). The global capacity for PCE/CTC from the 7 or 8 PCE/CTC plants is 360 Gg. In 2014, production of PCE from this process was 300 Gg, along with 39 Gg of CTC. PCE is also produced in one PCE/trichloroethylene plant (NAFTA), which uses $Cl_2$ as feedstock. This route does not involve CTC production or emissions. Furthermore, a small amount of PCE is made from the production of acetylene, but this process is unlikely to create CTC either.

***Table 1.*** *CM and PCE/CTC plants production capacity for 2014.*

| **Region** | **CMs production from CM plants[1]** | | | | **PCE/CTC production from PCE plants[1]** | | | | **Total CTC Production** |
|---|---|---|---|---|---|---|---|---|---|
| | Plants | CM Production | Actual CM Production | **Actual CTC** | Plants | PCE/CTC Production | Actual PCE Production | **Actual CTC** | |

| | Capacity | | production | Capacity | | Production | |
|---|---|---|---|---|---|---|---|
| **Europe** | 6 | 660 | 500 | **29.5** | 3 | 195 | 160 | **9** | **38.5** |
| **Russia** | 2 | 80 | 60 | **2.7** | | | | | **2.7** |
| **NAFTA** | 3 | 420 | 380 | **25** | 2 | 135 | 113 | **30** | **55** |
| **China** | 16 | 2150 | 1450 | **76.5** | 2-3 | 30 | 27 | **0** | **76.5** |
| **India** | 4 | 210 | 195 | **20** | | | | | **20** |
| **Japan** | 3 | 185 | 140 | **7** | | | | | **7** |
| **S Korea** | 1 | 80 | 60 | **3** | | | | | **3** |
| **Total** | 35 | 3785 | 2785 | **163.7** | 7-8 | 360(+) | 300 | **39** | **202.7** |

[1]*Sources and verifications: Nolan Sherry & Associates (NSA) database, European Union Directorate General Clima, US-Environmental Protection Agency, UN Comtrade (comtrade.un.org), Industry, UN Multi-Lateral Fund, World Bank Foreign Economic Cooperation Office, Montreal Protocol Technical and Economic Assessment Panel*

Figure 1 shows the CTC production from CM plants (164 Gg in 2014 in blue: capacity via this route is ~190 Gg and will probably increase in the future) and PCE/CTC plants (39 Gg in blue). Combining these 2 routes results in a 2014 estimated production of ~203 Gg. This is consistent with 2013 Technology and Economic Assessment Panel (TEAP) reported estimated production of 200 Gg [*UNEP*, 2013].

***Unreported non-feedstock emissions from CTC production (Fig. 1, Pathway B):***

The locations of currently operating CM and PCE/CTC production facilities are known and consist of 35 CM plants and 7-8 PCE/CTC plants globally (see Table 1). In addition, CTC may be generated inadvertently in other processes, as noted previously, where molecular chlorine comes into contact with a hydrocarbon, such as in the ethylene dichloride and vinyl chloride monomer production chain.

Fugitive CTC emissions from CM production with best industry standards can be less than 0.3%, but are higher in practice. Consequently, the 13.1 Gg emissions estimate (Table 2 and Fig. 1 Pathway B in top middle) is a weighted average (0.5%) of fugitive emissions in the production and supply chain in different parts of the world. (Source: multiple discussions over years with producers). Fugitive emissions from PCE/CTC plants are estimated to be negligible (see previous discussion on PCE/CTC plants).

***Table 2.*** *Estimated unreported non-feedstock emissions from CTC production in CM and PCE plants (left, Fig. 1 Pathway B) and fugitive emissions from incineration, feedstock uses, and process agent use (Fig.1, Pathway C) for 2014. Colors are as those shown in Figure 1. DVAC is divinyl acid chloride, which is one of the precursors to cypermethrin.*

| Region | Figure 1 Pathway B | | Figure 1 Pathway C | | | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *From CM plants* | *From PCE plants* | ***(i) Incineration*** | | ***(ii) PCE production*** | | ***(iii) HFC production*** | | ***(iv) DVAC Production*** | | ***(v) MeCl production*** | | ***(vi) Process agent*** | | |
| | | | *Usage* | *Emis.* | *Usage* | *Emis.* | *Usage* | *Emis.* | *Usage* | *Emis.* | *Usage* | *Emis.* | *Usage* | *Emis.* | |
| **Europe** | 2.01 (0.4%) | 0 | 15 | 0 | 16 | 0 | 7 | 0 | | | | | 0.5 | 0.01 | **2.0** |
| **Russia** | 0.44 (0.7%) | 0 | 2.2 | 0 | | | | | | | | | 0.5 | 0.2 | **0.6** |
| **NAFTA** | 1.56 (0.4%) | 0 | 1.5 | 0 | 21.5 | 0 | 30.5 | 0 | | | | | 1.5 | 0.04 | **1.6** |
| **China** | 6.55 (0.5%) | 0 | | | 27 | 0.2 | 20 | 0.2 | 3 | 0.1 | 26 | 0.2 | 0.1 | 0.05 | **7.3** |
| **India** | 1.78 (0.9%) | 0 | | | | | | | 20 | 1 | | | | | **2.8** |
| **Japan** | 0.56 (0.4%) | 0 | 7 | 0 | | | | | | | | | | | **0.6** |
| **S Korea** | 0.24 (0.4%) | 0 | 3 | 0 | | | | | | | | | | | **0.2** |
| **Total** | **13.14 (0.5%)** | **0** | **28.7** | **0** | **64.5** | **0.2** | **57.5** | **0.2** | **23** | **1.1** | **26** | **0.2** | **2.6** | **1.3** | **15.1** |

## C. CTC current usage and emissions

CTC had a number of uses in the past, primarily as a feedstock for the production of chlorofluorocarbons. Current uses are now confined by the Montreal Protocol to be in contained processes. As shown in Table 2, industrial production of CTC in 2014 was consumed in: (i) incineration (29 Gg); (ii) as a PCE feedstock (64 Gg); (iii) as HFC feedstock (58 Gg); in (iv) methyl chloride (MeCl) production (26 Gg); (v) in divinyl acid chloride (DVAC) production (23 Gg); and (vi) for use as process agents and laboratory purposes (3 Gg). This consumption is illustrated in Figure 1 with the lighter blue bars. As CTC is used as feedstock (>95% of total production), most gets converted to other products, like HFCs, PCE, etc. CTC is still used as a process agent and in laboratory applications (Fig. 1 vi), but in relatively small amounts of 3 Gg/year globally.

***Fugitive emissions from usage of CTC (Fig. 1, Pathway C):***

(i) Incineration does not generate emissions of CTC. Approximately 29 Gg was incinerated in 2014 (see Table 1), from which we assume none was emitted.

(ii) CTC is used as feedstock to produce PCE in PCE-from-CTC plants (2-3 plants in China). The process involves the co-reaction of methane, chlorine and CTC (e.g., $CCl_4 + 4\ Cl_2 + CH_4 \rightarrow C_2Cl_4 + 4\ HCl$). This production process should be CTC emission-free. In some cases, the CTC is road-shipped from CM producers, resulting in potential fugitive leakage during transport and storage. We assume some transport leakage, storage leakage, and production fugitives, therefore a small amount (0.2 Gg in 2014) has been added to the emission estimate from the PCE-from-CTC production route in China.

In China, there is no permit to operate CM plants unless CTC is demonstrably used as a chemical intermediate. However, the heavy tars containing CTC from CM plants may (illegally) be sold as bitumen thinner or sleeper/telegraph pole protection. There is limited knowledge on heavy CTC tars disposal.

(iii) Production of hydrofluorocarbons (HFCs) and hydrofluoroolefines (HFOs) uses CTC in the "Kharasch" process in relatively new plants. The earliest operation started in mid-1990s, one or two in the 2000-2009 period, and about three in recent years. HFC-245fa and HFC-365mfc are made by this process. These HFCs are produced in relatively small absolute volume by large chemical companies that follow best industry practice. We have estimated a small default as fugitive emissions (0.2 Gg in 2014). Note the overall CTC demand for HFC/HFO feedstock should increase by at least 50% in the coming years. This is because HFO-1234yf, which is also produced from CTC, is likely to replace HFC-134a, which does not use CTC, in automotive air-conditioning.

(iv) Methyl chloride (MeCl) is generally made globally by reaction of methanol with HCl but 2-3 companies (in China) produce MeCl by dehydrochlorination of CTC. The product may contain some methanol but does not carry CTC traces (nor other higher CMs), which would destroy upstream products. We have assumed 0.2 Gg of fugitive emissions in 2014 from this production process.

(v) Divinyl acid chloride (DVAC) production consumes CTC in a Kharasch reaction with acrylonitrile, as the starting point in a 10-stage process to make synthetic pyrethroids (10 plants in India, one plant in China). In India, DVAC production controls the demand for CTC. As trucks carry all of the CTC from the production sites to the producers, with the

resulting potential for emissive losses, we included both double storage and transport fugitive emissions of 1.1 Gg in 2014.

(vi) CTC is used as a process agent and in laboratory and analytical uses all of which must be agreed, on a case by case basis, by the Parties to the Montreal Protocol. We have made the pessimistic assumption that 10% of the use (agreed by the parties to the Montreal Protocol) will be emitted, which results in 0.3 Gg emissions in 2014.

**D. Legacy emissions from landfills and contaminated sites**

While the current CTC uses are detailed in Section C, historic uses of CTC for various processes were widespread, and contaminated CTC was typically disposed of in an environmentally careless manner. Historic CTC applications included metal degreasing, dry-cleaning fluid, fabric spotting, fire extinguishing, grain fumigation, and uses as a reaction medium [*Holbrook*, 2000]. These early disposal practices led to a number of "legacy" sites that have continued emissions (*e.g.*, see *Truex et al.* [2001]). These legacy emissions (*i.e.,* emissions from old industrial sites and landfills) may also be important to the global overall CTC emissions (Fig. 1, Pathway D). *Fraser et al.* [2014] estimated that unaccounted CTC emissions (legacy emissions and from chlor-alkali plants) could potentially contribute 10-30 Gg/year globally. Based on newly available information, *SPARC* [2016] revised this estimate to 5-10 Gg/year. This estimate is highly uncertain, however, as it is upscaled from Australian emissions to the global level.

Recent CTC emissions estimates using atmospheric observations over the United States (U.S.) by *Hu et al.* [2016] suggest that the U.S. emissions distribution is very similar to the distribution of chlor-alkali plants in the U.S.. However, these results could not be used to identify the importance of these plants for CTC emissions (Pathway A) relative to other industry-related sources such as CM and PCE (Pathway B). Inadvertent CTC emissions from chlor-alkali plants have not been rigorously assessed globally. Furthermore, a similar study of European CTC emissions by *Graziosi et al.* [2016] showed these to be about 4% of global emissions and suggested that regions with large producers of basic organic chemicals were significant sources of CTC emissions. Combined emissions from legacy sources and chlor-alkali plants have been estimated to be ~10 Gg in 2014.

**Summary**

CTC emissions have been estimated using top-down techniques from observations (35 Gg/year) and from a bottom-up technique that utilizes Montreal Protocol based reports to UNEP (3 Gg/year) in *SPARC* [2016]. This large discrepancy between the top-down and bottom-up estimates suggests uncontrolled CTC emissions.

An analysis of CTC sources from consideration of industrial processes in 2014 was completed as part of *SPARC* [2016]. In that report, four potential sources were identified; Pathway A) unreported but inadvertent emissions from chlorine gas usage and chlor-alkali plants; Pathway B) unreported non-feedstock emissions from industrial production that includes CTC: ~13 Gg; Pathway C) fugitive emissions from known feedstock usages, incineration, and process agents/laboratory: ~2 Gg; and Pathway D) legacy emissions from

landfills and contaminated soils: together (A) and (D) could be as high as 10 Gg. In sum, these four sources were estimated to be up to 25 Gg in 2014, an amount that is considerably larger than 3 Gg of emissions inferred from UNEP reported CTC production.

The non-feedstock emissions from CM and PCE/CTC production and the inadvertent emissions associated with the production and use of chlorine gas have so far not been included in the bottom-up estimates for the WMO/UNEP Scientific Assessments of Ozone Depletion [*e.g.*, WMO, 2014] and hence contribute considerably to closing the gap between bottom-up estimates and top-down calculated emissions.

This amount of 25 Gg/year is however still lower than the average of the estimated emissions of 35±16 Gg/year related to global trends of CTC in the atmosphere and current best estimates of CTC lifetimes in air, sea water and soil. Narrowing this budget gap will require additional research as noted in the Research Suggestions section of *SPARC* [2016].

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